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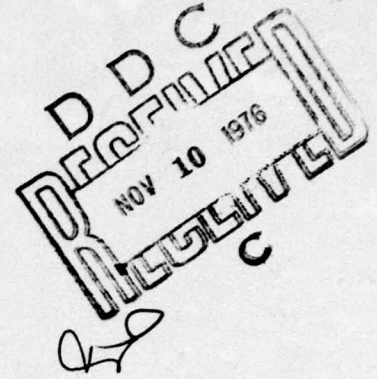
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NAVAL POSTGRADUATE SCHOOL  
Monterey, California



THE DESIGN AND CONSTRUCTION OF A  
STOPPED-FLOW APPARATUS

Kenneth J. Graham

Richard A. Reinhardt

September 1976

Final Report for Period July 1970 - September 1976

Approved for public release; distribution unlimited.

Prepared for:

Chief of Naval Research, Arlington, Virginia 22217, and  
Naval Postgraduate School, Monterey, California 93940.

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*Richard A. Reinhardt*  
 RICHARD A. REINHARDT  
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# THE DESIGN AND CONSTRUCTION OF A STOPPED-FLOW APPARATUS

by

Kenneth J. Graham and Richard A. Reinhardt

## Preface

This report deals with the stopped-flow apparatus, constructed locally over the period from 1970 to 1974 as part of the research project entitled "Ammine Complexes of Palladium". Herein are documented the history of the fabrication and considerable detail on the design of the present working model, including modifications planned for the immediate future. Also included are quite detailed operating instructions intended for the benefit of anyone desiring to operate the instrument. It is intended, toward the latter end, to provide updated instructions from time to time.

## TABLE OF CONTENTS

I.	THE STUDY OF RAPID REACTIONS IN SOLUTION - - - - -	7
1.	Continuous Flow - - - - -	7
2.	Stopped-Flow Methods - - - - -	9
II.	EVOLUTION OF STOPPED-FLOW REACTORS AT THE NAVAL POSTGRADUATE SCHOOL - - - - -	11
1.	General Remarks - - - - -	11
2.	Prototype Model I - - - - -	11
3.	Prototype Model II - - - - -	13
4.	Prototype Model III - - - - -	15
5.	Salient Features of the Present Working Model IV - - -	15
III.	DESIGN AND OPERATION OF THE REACTOR - - - - -	21
1.	Reservoir Valves - - - - -	23
IV.	OPTICS AND ELECTRONICS - - - - -	24
V.	CALIBRATION - - - - -	25
1.	Calibration Reactions - - - - -	25
2.	Transport Time - - - - -	26
3.	Efficiency of Mixing - - - - -	26
VI.	ERRORS - - - - -	27
1.	Slit-length and Finite-mixing-time Errors - - - - -	27
2.	Diffusion - - - - -	28
3.	Inequality of Flow - - - - -	28
4.	Cavitation - - - - -	28
5.	Air Bubbles - - - - -	29



VII.	APPENDIX A: OPERATING CHARACTERISTICS OF THE	
	MODEL IV REACTOR - - - - -	30
VIII.	APPENDIX B: DETAILED OPERATING INSTRUCTIONS - - - - -	35
IX.	APPENDIX C: PARTS LIST AND SUPPLIERS - - - - -	42
X.	REFERENCES - - - - -	44



# LIST OF ILLUSTRATIONS

Figure no.		Page no.
1.	Continuous Flow Schematic - - - - -	8
2.	Generalized Stopped-Flow Schematic - - - - -	9
3.	Prototype Model I - - - - -	12
4.	Prototype Model II - - - - -	14
5.	Prototype Model III - - - - -	16
6.	Variable Diameter Teflon Pistons - - - - -	17
7.	Model IV Schematic - - - - -	18
8.	Perspective drawing of Stopped-Flow Reactor, Model IV - - - - -	19
9.	Assembled Stopped-Flow Reactor, Model IV - - - - -	20
10.	Overall view of Stopped-Flow Apparatus - - - - -	32
11.	Detail of the Electronics Package - - - - -	33

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The late Robert Scheile, Supervisory Machinist, whose creativity and drive made possible the design of Models III and IV. We continue to feel, privately as well as professionally, the great loss occasioned by his untimely death in 1974.

Robert C. Smith of the Research Electronics Shop for his constant general electronic assistance and, in particular, for the construction of the new detector amplifier.

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many hours in the necessary testing which ultimately proved the unsatisfactory nature of Model III.

LCDR Ross G. Hibler, whose master's thesis research involved the actual and successful operation of the Model IV reactor.

Our apologies are extended for failing to mention the many others whose assistance, great or small, was also needed for the completion of this instrument.



## THE STUDY OF RAPID REACTIONS IN SOLUTION

Techniques for the investigation of chemical reaction rates can be classified roughly into two sorts: "conventional (or classical) methods for reactions with half-lives of a few sec and upwards; and rapid-reaction methods for faster reactions down to the nsec range. Conventional methods are limited in time resolution by the rate of mixing, typically by mechanical shaking or stirring of reactants.

Rapid-rate techniques overcome this limitation in one of two ways. In flow methods, turbulence is set up as reagents flow through a mixing device, allowing for very rapid and efficient mixing. Resolution times to tenths of a msec are thus available. In relaxation methods (not to be discussed further in this report [1]) a system initially at equilibrium is perturbed by a sudden change in pressure, temperature, or concentration and the return to equilibrium is followed by the change in some physical property. Relaxation methods can be used to study processes down to the nsec range. Excellent surveys of rapid-rate methods are to be found in the literature [1,2,3,4] with many experimental details provided.

### Continuous Flow

The earliest flow methods were by the continuous-flow technique [5]. The two solutions, as shown in Figure 1, are forced into a mixing chamber, M, travelling with a velocity,  $u$ , of several  $\text{m sec}^{-1}$ . Observation is made of some physical property at O, which is at a distance  $d$  from the mixing chamber. Thus

the age of the mixed system (the reaction time) is given by  $d/u$ , and data at different times may be obtained by varying either  $d$  or  $u$ . So long as steady flow continues, and so long as  $O$  is beyond the region of non-homogeneous mixing, the composition at  $O$  is fixed and thus measurements can be made comparatively at leisure.

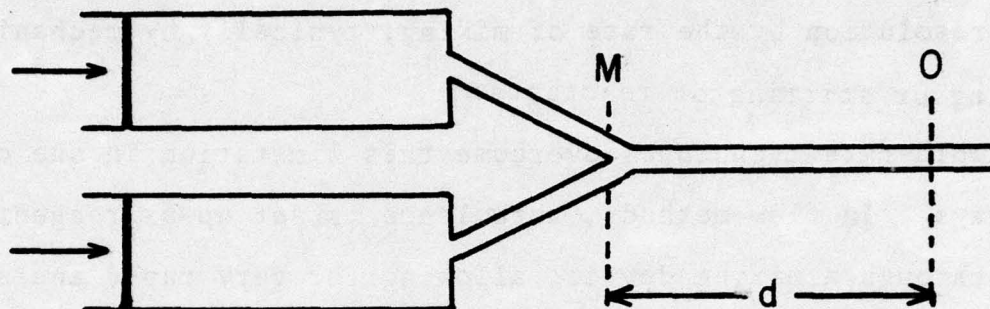


Figure 1. Continuous Flow

Effective mixing, however, does require turbulence at the point of mixing, and it is easily seen that there is consequently the requirement for a large expenditure of reagents. Empirically it is found [2, p 715] that for turbulent flow the dimensionless Reynolds number must exceed 2000. This is equivalent to the condition that for flow of a liquid of viscosity  $\eta$ , density,  $\rho$ , in a tube of radius  $r$ , the flow velocity  $u$  must exceed  $1000 \eta/\rho r$ . Converted to volume flow, with water we obtain the expression  $dV/dt \approx 30r \text{ cm}^3 \text{ sec}^{-1}$  ( $r$  in cm) or about  $2000r \text{ cm}^3 \text{ min}^{-1}$ . For example, in the 1923 measurements of Hartridge and Roughton [5] several liters of solution were required per experiment. By using more rapid detection devices,



these volumes can be significantly reduced [4, p 33] but then the chief advantage over stopped-flow equipment has been largely lost.

### Stopped-Flow Methods

In this technique, two reactant solutions are rapidly mixed by flowing through a mixer, as in continuous flow, but then the flow is suddenly stopped (e.g., within a msec or so). An element of solution a short distance (say, 1 cm) from the mixing chamber will have been mixed for a few msec: the age of the first observed sample is the dead time of the equipment. Subsequent reaction of this element is then followed by rapid observation of some physical property -- typically, the absorption of light, detected by a photomultiplier and displayed on an oscilloscope.

Although there are early uses of the technique reported by Roughton [6] and Chance [7] extensive use of stopped-flow methods dates from Gibson's use of a stopping piston [8]. In Figure 2, Gibson's device is shown schematically. Solutions in syringes A and A' are rapidly mixed by the flow through M. The stopping piston, P, is pushed along by the reaction mixture and is

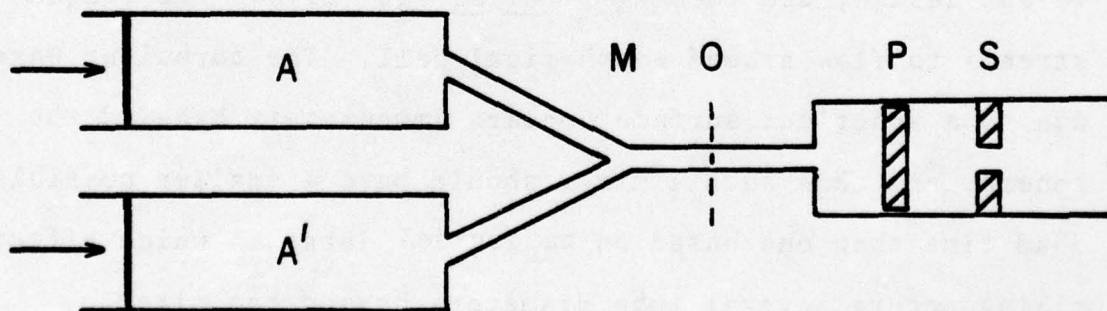


Figure 2. Generalized Stopped-Flow



suddenly halted by coming up against an external stop, S. Observation is at point O. The flow must be stopped very suddenly for the following reason: if the flow is too slow, the efficiency of mixing falls off badly; and thus if the flow were stopped gradually, the liquid which came to rest at O would be incompletely mixed.

Stopped-flow equipment can yield resolution times down to the msec range. Small volumes of solution are adequate. There is, on the other hand, the requirement for rapid observation and the more complex electronics associated therewith.

In flow systems of either kind, it is necessary that the reagents be mixed thoroughly and as rapidly as possible, so that there are no inhomogeneities at the location (or time) of the earliest observations. Typical of the design is that of Gibson and Milnes [9] in which the reagents enter through eight jets of  $\frac{1}{2}$ -mm diameter, opening tangentially into a central mixer tube of 2-mm diameter. The jets are so placed that the two series tend to spiral the liquid in opposite directions. Such design tends to maximize turbulence, yet avoids the violent spinning which could lead to cavitation. A somewhat different design, due to Berger, et al [10] allows the reagent streams to flow around a spherical ball. The turbulent wake due to a spherical surface appears immediately behind the sphere, and thus such a mixer should have a smaller possible dead time than one based on tangential jets, in which effective mixing occurs several tube diameters beyond the mixer.

## EVOLUTION OF STOPPED-FLOW REACTORS AT THE NAVAL POSTGRADUATE SCHOOL

### General Remarks

We shall employ the term "stopped-flow reactor" to refer to the rapid-mixing device with all the associated conduits and mechanical controls, but not including electronic or optical components. The entire system will be referred to as "stopped-flow apparatus". A series of reactor models was constructed in this laboratory in the period from 1970 to 1973 for testing of design features. In addition to those noted below, after the construction of Model I, tests were made on a variety of mixer designs with regard to feasibility of construction and to mixing characteristics as observed visually.

### Prototype Model I (1971, see Figure 3).

This model made use of independent modular units. The mixer was of cast polyester, following Berger's [10] spherical design. Solutions were conducted to the mixer by external lengths of tubing. The silica observation cell, of 2-mm square cross-section, was attached directly to the mixer. Observation was made perpendicular to the direction of flow, resulting in a very short optical path.

Liquid drive was effected by means of gas-tight glass syringes, pneumatically operated. Stopping was against a vernier micrometer, with an adjustable-leaf microswitch to trigger the oscilloscope.

A number of problems were associated with Model I. The very short light path was a clear disadvantage. The construction was



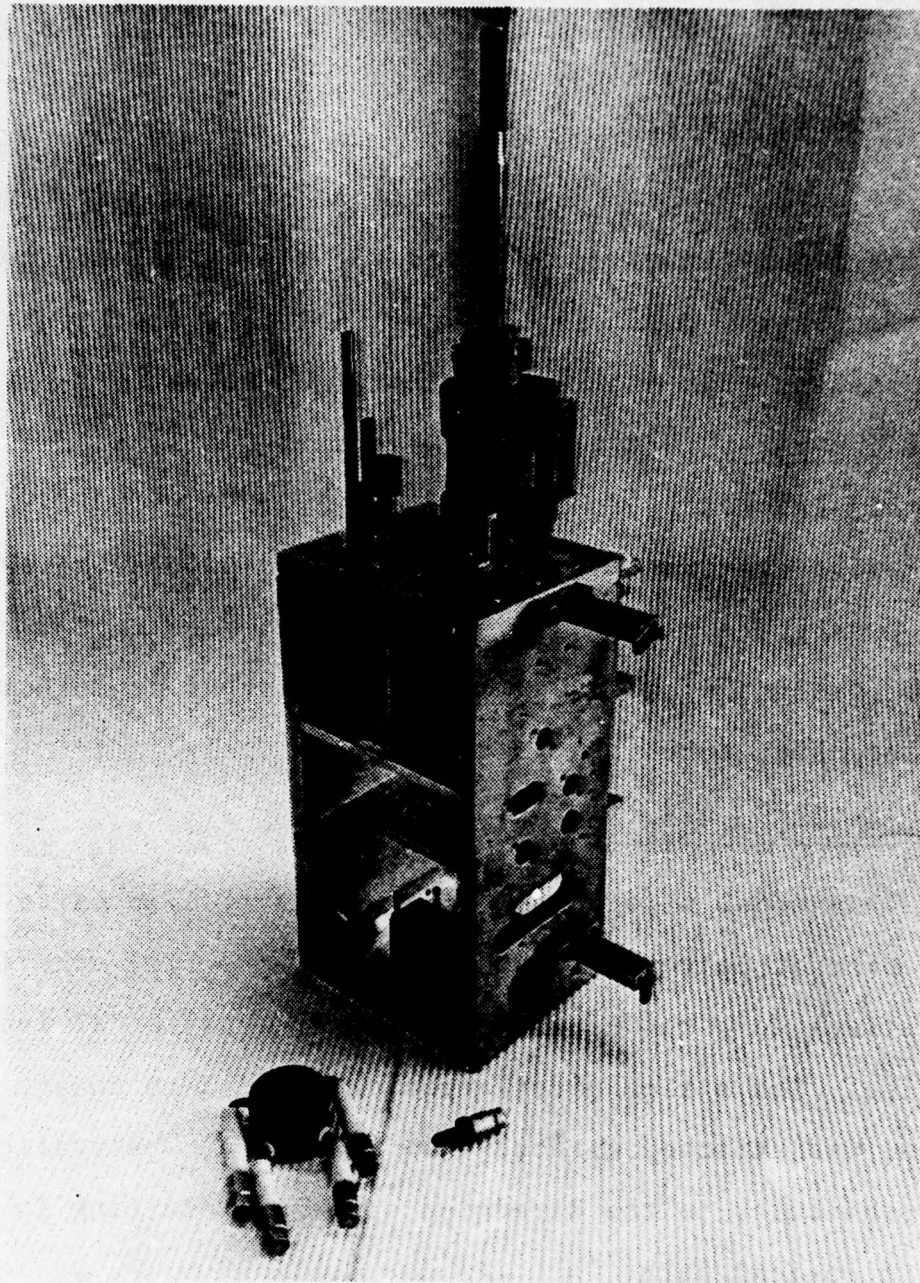


Figure 3. Prototype Model I



bulky and clumsy, with many valves to be operated and much tubing running around; as a result, there were many leaks. The stopping was imprecise ("bouncy") due to lack of rigidity in the Teflon tubing, especially that leading to the stopping cylinder.

#### Prototype Model II (1971, see Figure 4)

This was constructed of laminated Lucite, each lamina containing a layer of the channels of the flow system, and the whole cemented together. Avoiding the difficult machining of the Berger mixer of Model I, a mixer based on that in the commercial Aminco-Morrow [11] stopped-flow apparatus was used. In this, the two reagents are brought together into the mixer as opposed jets and the mixed reagents are split and then are finally recombined. Observation, which begins immediately beyond this last mixing, is parallel to the direction of flow, a nearly 4-cm optical path being used. Cell windows were cut from glass microscope slides.

Liquid drive was accomplished with plastic syringes, the plungers being provided with rubber seals; it was hand operated. The stopping syringe, in a separate housing from the mixer proper, operated against a micrometer screw.

Problems associated with this model were: non-reproducible flow rate due to the manual operation; "bouncy" stopping on account of the plastic tubing leading to the stopping assembly and to the plasticity of the various syringes; rusting of the metal guide bars.

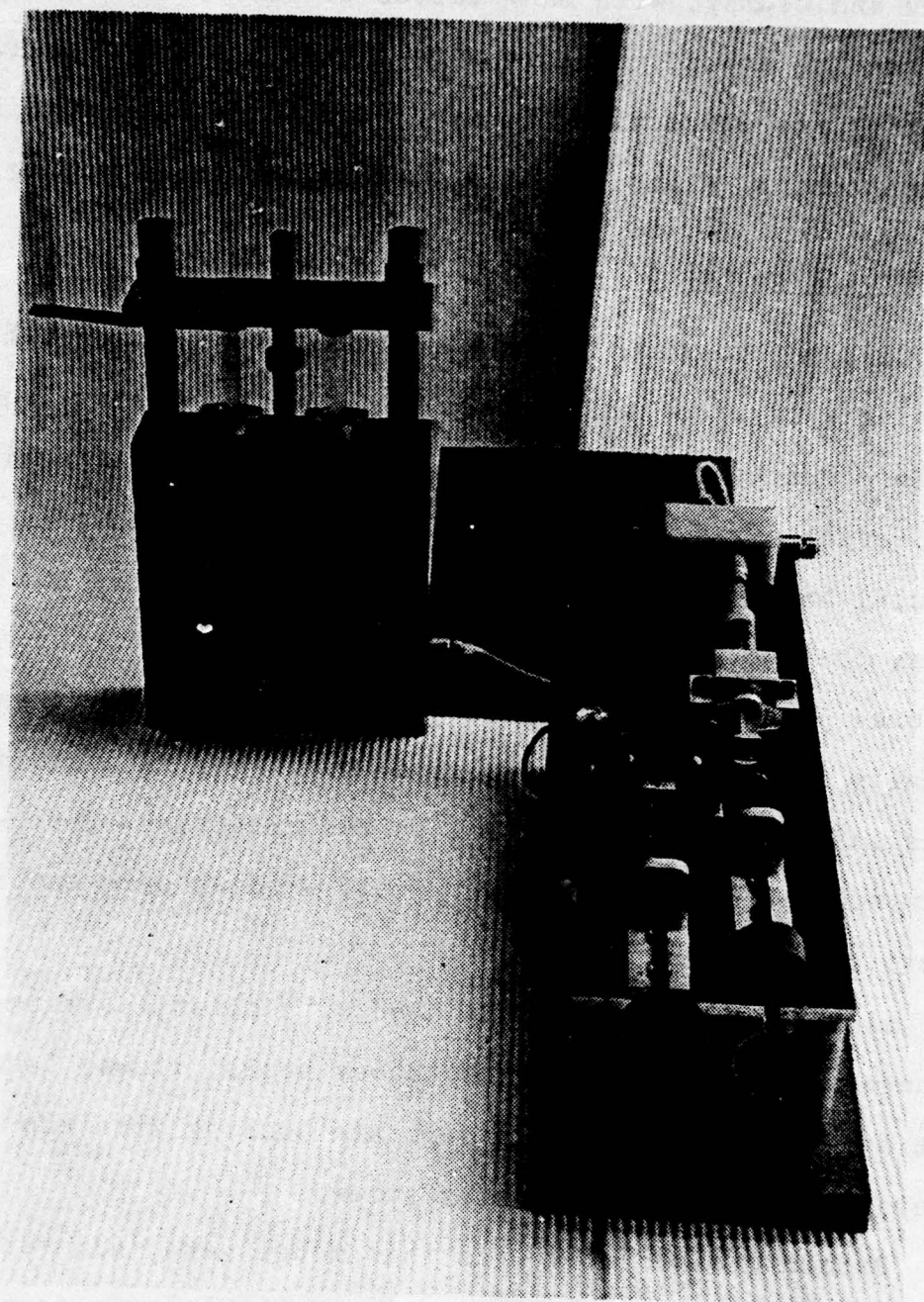


Figure 4. Prototype Model II



### Prototype Model III (1971-72, see Figure 5)

This represents a realization of the design features tried out in Model II and was, in fact, a working model used well into 1973. To avoid the oscillations in stopping, the stopping cylinder was included in the laminated block along with the driving cylinder, mixer, and observation port. Drive was by means of piston-type syringes operated pneumatically. To attempt to compensate for leaks, the Teflon pistons were made in such a way that the diameter could be slightly increased (see Figure 6). The syringe bores were lined with either glass or polypropylene. The mixer was identical to that of Model II.

The principal difficulties with Model III were with the drive syringes. The glass liners broke frequently, a result presumably of some part slightly out of line. Polypropylene liners, while of adequate resilience to avoid this problem, tended to seize badly when the plungers were tightened enough to prevent leaks. It may be remarked also that attempts to use nylon for valves were unsuccessful, as the material showed marked deterioration when wet with 1 M perchloric acid and then exposed to air for a time.

### Salient Features of the Present Working Model IV (1973-74)

This unit, shown schematically in Figure 7 and in detail in Figs. 8 and 9, was constructed of solid Lucite, not laminated, as there had been some tendency in Models II and III for leaks to develop between the laminae after extended use. The various flow channels were made by machining and plugging as required.

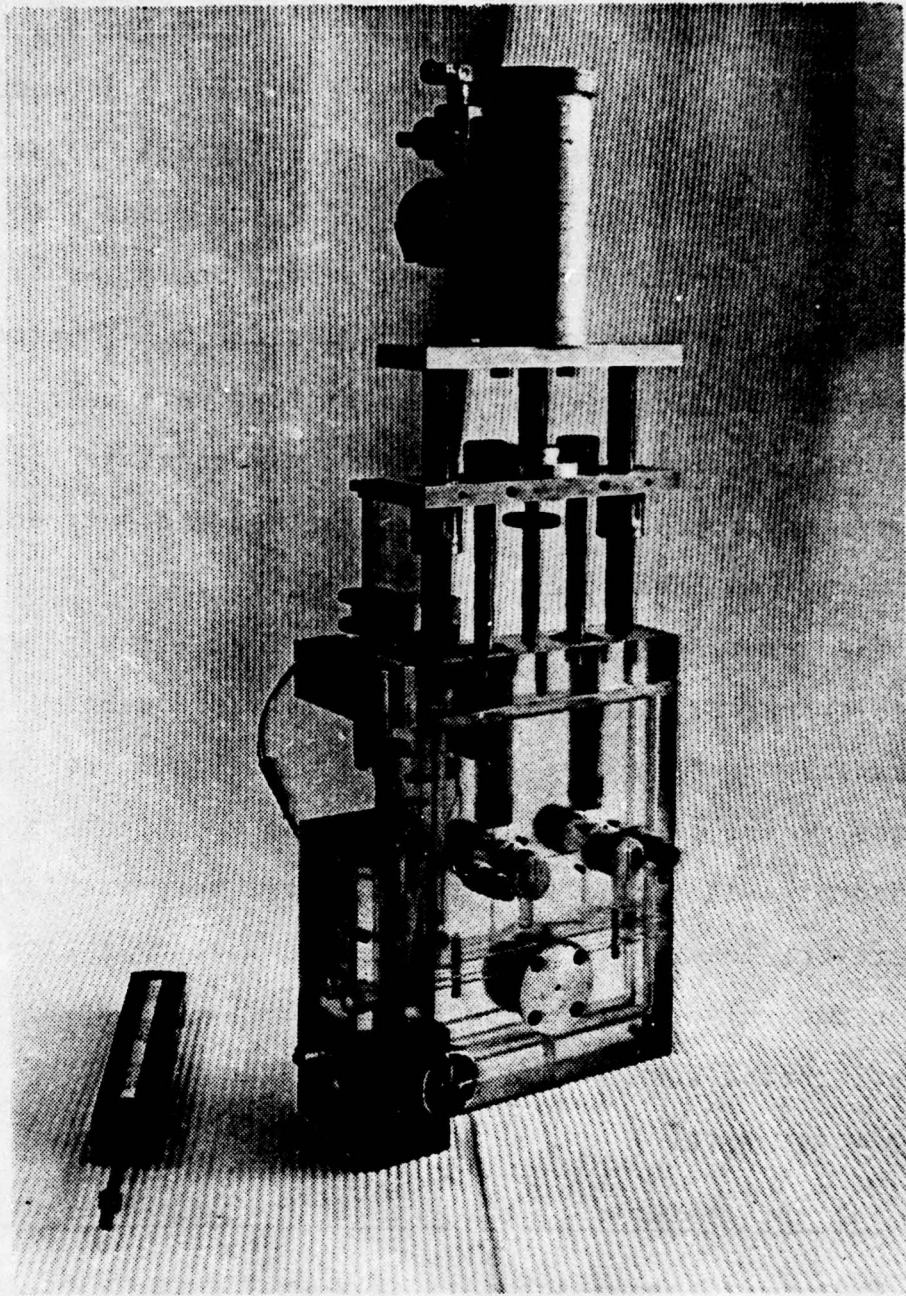


Figure 5... Prototype Model III



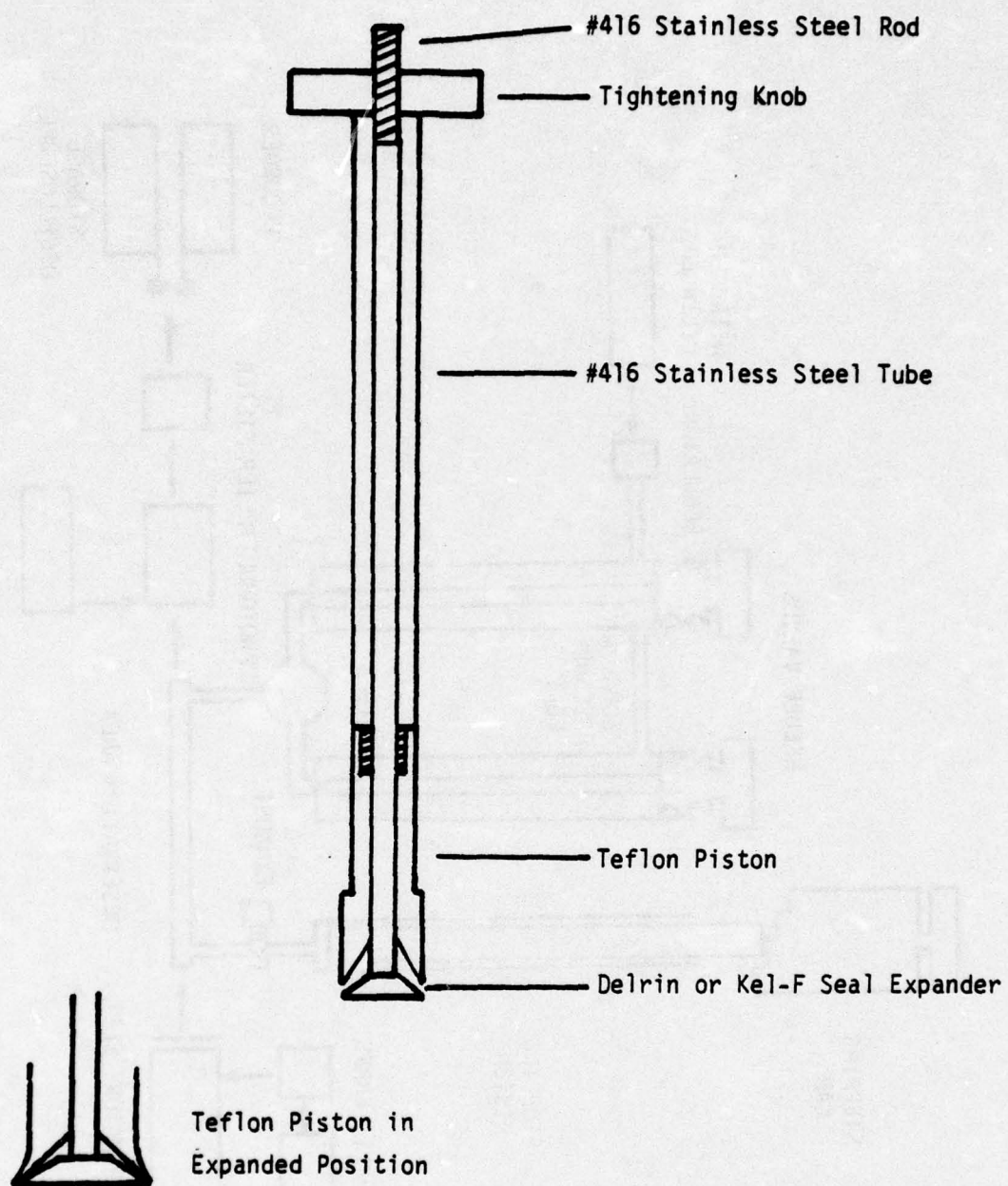


Figure 6. Variable Diameter Teflon Pistons

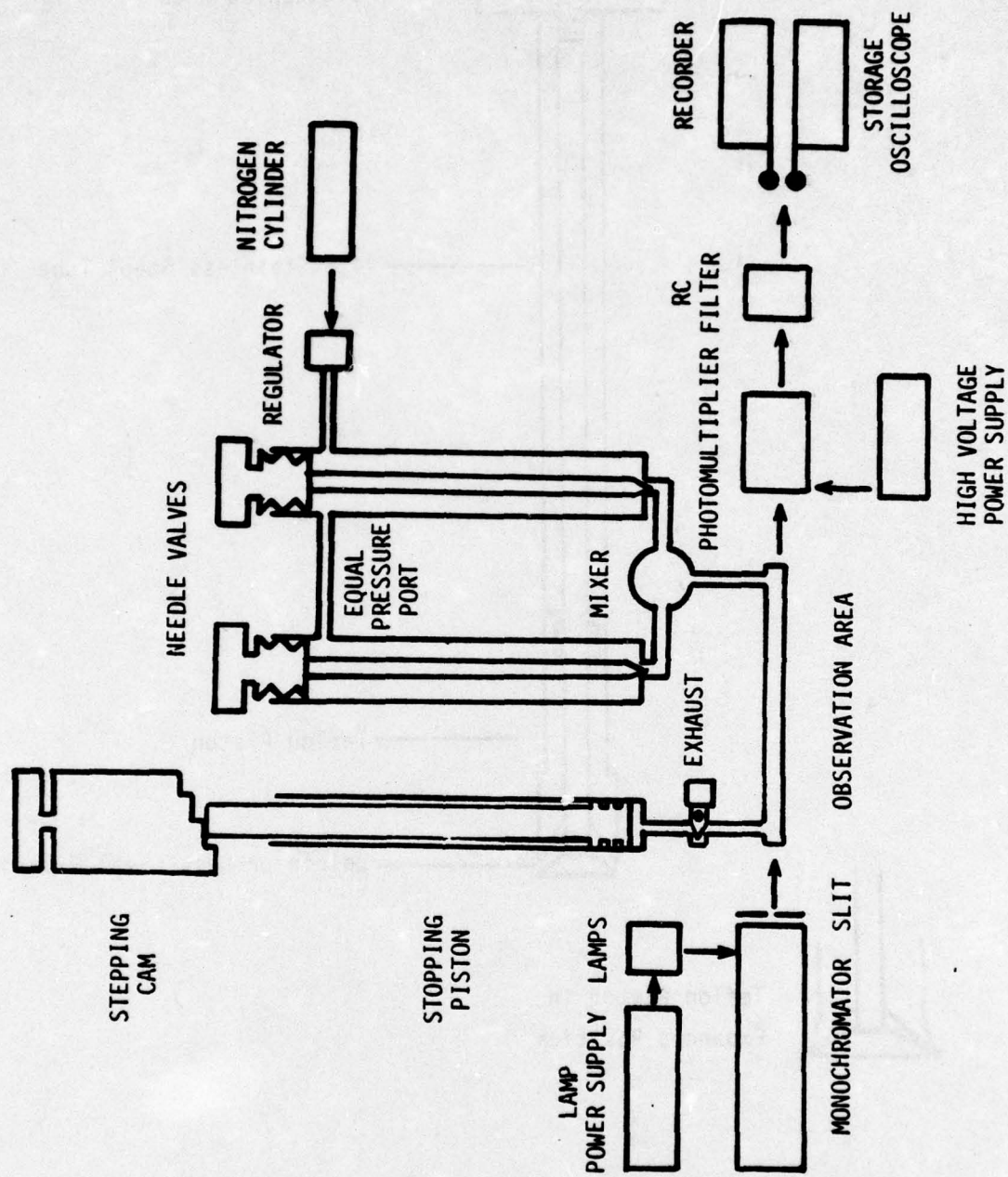


Figure 7. Model IV Schematic



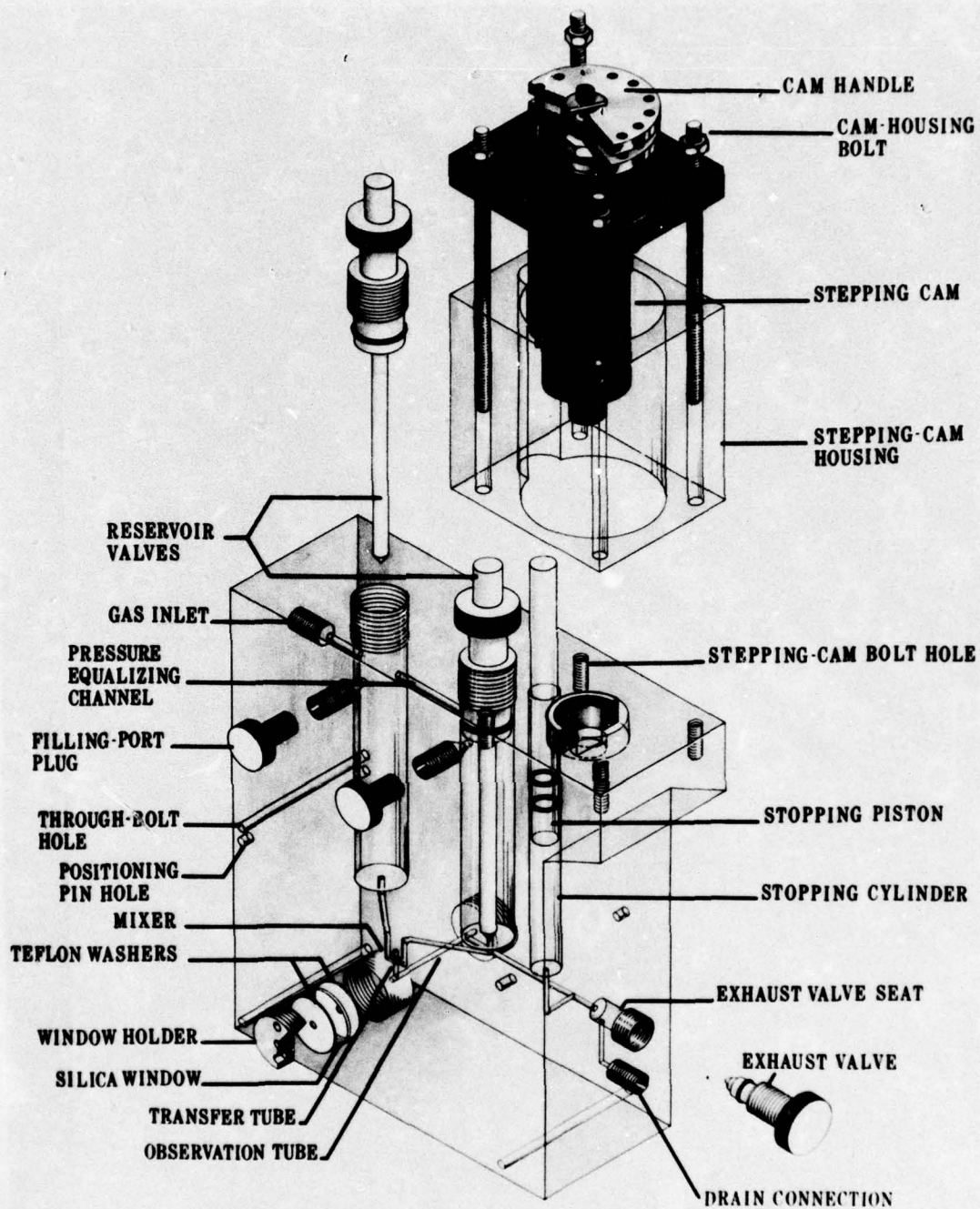


Figure 8. Perspective drawing of Stopped-Flow Reactor, Model IV.

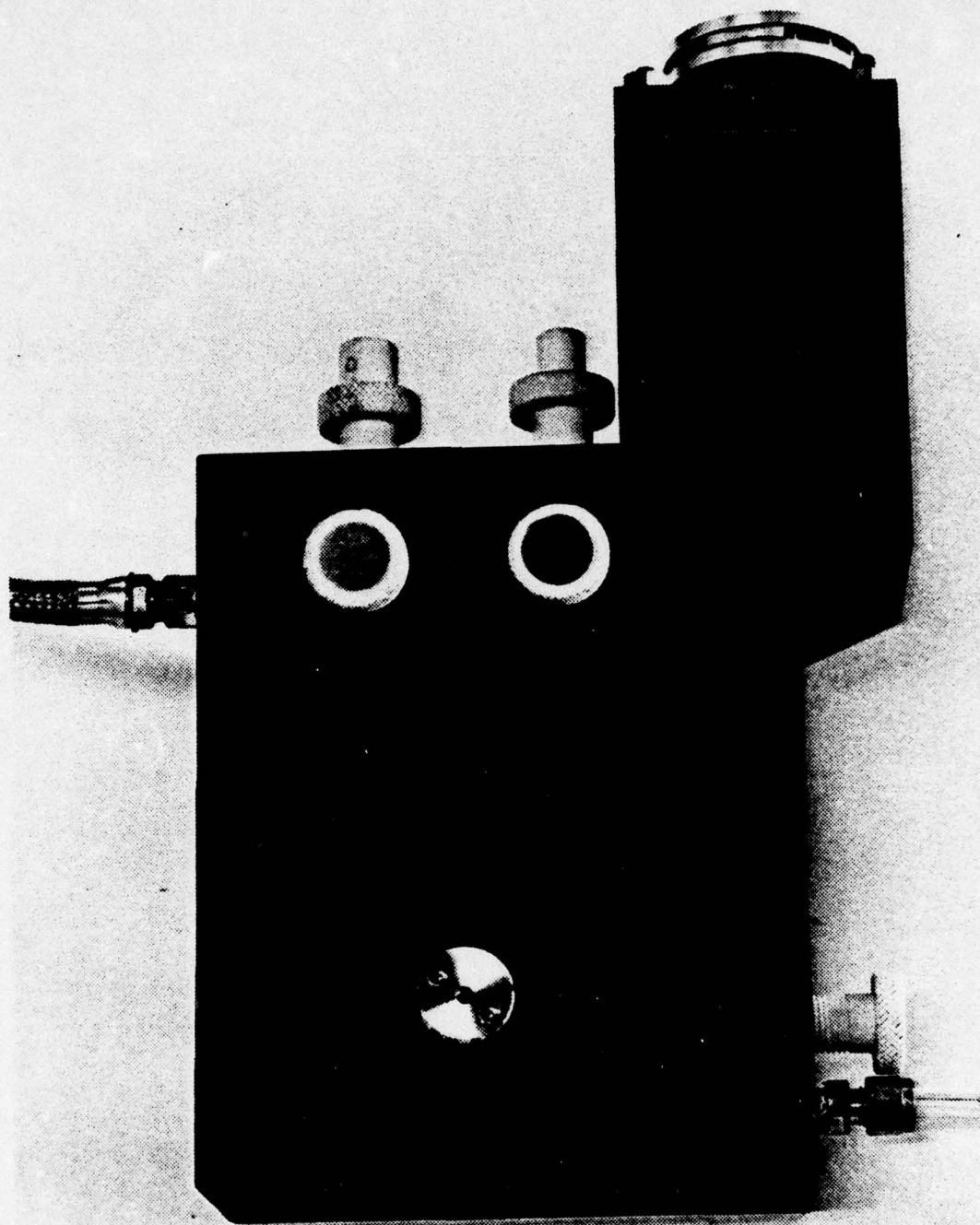


Figure 9. Assembled Stopped-Flow Reactor, Model IV



The mixer is essentially of the original Gibson [9] design; elimination of the splitting and remixing of the previous model effected a very considerable reduction in dead time. The mixer was constructed on a Lucite rod which was inserted into a machined hole in the Lucite block and cemented in place.

Liquid drive is by gas (nitrogen) pressure acting directly on the reagents, which are held in cylindrical reservoirs. (In this way the drive problems noted in Model III are eliminated.) Necessary control valves are of Teflon. Observation of the mixed solution is along the direction of flow.

In the stopping device, a Lucite stopping piston comes up against the stepping cam (see figure 8), an arrangement which allows up to twelve shots to be made in rapid succession.

#### DESIGN AND OPERATION OF THE REACTOR

Figure 8 shows the present\* reactor in exploded configuration. The reactor housing is of a single block of Lucite, about 18 cm long at the top, 19 cm high and 6 cm thick. The entire exterior is painted flat black with a nitrocellulose lacquer. Interior channels in the mixer section are of 2 mm diameter; other dimensions can be estimated from Figure 8, which has a scale of 0.357:1.

The two storage reservoirs are filled from the front by

---

\*This figure shows the original needle-valve design. The pending modification is discussed in the section "Reservoir Valves".

\*\*Detailed plans are available on request.

removal of the threaded-in Teflon plugs. Gas pressure can be applied by making use of the threaded opening to the left which will accept a pipe fitting. The two reservoirs are connected above the maximum liquid level by a pressure-equalization channel. The Teflon needle valves serve to seal off the reservoirs from the mixing section immediately below.

The mixer is designed closely after that of Gibson and Milnes [9; 3, p 192] but with the number of jets being reduced from eight to four. Thus jets of each solution enter tangentially at two different levels.

A short transfer tube leads to the observation tube, which starts just below the mixer and extends 4 cm to the rear portion of the housing. A fused-silica window is at either end of this tube, each being threaded in using Teflon seats.

The stepping-cam housing is of Lucite, also painted black, and is secured to the upper right hand portion of the reactor at the four bolt holes shown in Figure 8. The stepping cam itself is made of brass. The projecting portion of the stopping piston is constrained to ride in the semicircular channel in the stepping-cam housing. The upper end of the piston rests against whichever step of the cam has been placed in position. When the lowest step is used, the bottom of the piston rests against the bottom of the stopping cylinder.

The exhaust valve, shown in the lower right of Figure 8, is a Teflon needle valve which when open allows liquid to flow from the stopping cylinder and from the mixing system out through the exhaust port.



The general mode of operation is as follows. (See Appendix B for details.) When the system is pressurized, the reservoir needle valves being open and the exhaust valve closed, solution will extend into the stopping cylinder so far as to force the piston to the limit imposed by the cam. A firing is then accomplished by turning the stepping cam to its next position, allowing a volume of solution to be forced by the gas pressure through the mixer, and thereby pushing the piston to its new position on the cam. Succeeding shots can be made in rapid succession by further rotation of the cam. At the conclusion of twelve shots, the piston will be at its highest position. The stopping cylinder is then emptied by closing the reservoir valves, opening the exhaust valve, and forcing down the stopping piston with a ramrod which fits through a hole in the top of the cam assembly. If the reservoirs have not been depleted, a further series of twelve shots can be made at once.

#### Reservoir Valves

The present needle-valve mechanism, as shown in Figure 8, has proved awkward in use due to the difficulty in turning the valves when the system is under pressure and to the virtual impossibility of ascertaining that the two valves are opened simultaneously. For this reason, a new mechanism has been designed and is under construction. In the modified design, a stationary Teflon bushing is fastened by the threads at the top of the reservoir. The valve itself, which is of Teflon reinforced internally with a stainless steel rod, slides inside the bushing, sealed by two O-rings. Atop the reactor housing

is affixed a metal yoke operated by a lever and cam. The valves are forced up against this yoke by springs. By the motion of the lever, the valves are simultaneously moved from open to closed or the reverse. Screws are inserted into the yoke to permit exact adjustment of the closed-valve position.

#### OPTICS AND ELECTRONICS

The optical system is a dedicated Beckman DU spectrophotometer system. Tungsten and hydrogen lamps are both available; with our particular equipment it is found that the tungsten lamp, where usable, gives a more stable illumination. The line-operated Beckman lamp power supply is used, providing excellent voltage regulation for either lamp. The spectrophotometer itself serves as the prism monochromator, with the optical path of the stopped-flow reactor in the place of the usual sample cell. Because of the small cross-section ( $0.03 \text{ cm}^2$ ) of the optical path, it is necessary to operate with the slit wide open at 2 mm, even though this causes a severe reduction in spectral resolution. The sliding filter has been converted to a shutter by an opaque insert in one of the positions.

Signal detection is by means of a photomultiplier. Presently, the system uses an end-on tube, either the RCA 7102 for use in the red spectral region or the RCA 6810A for use in the blue. In the immediate future the side-on tube RCA 4832 will be used. This has, in addition to the advantage of improved mechanical stability, a very flat response curve from the near ultraviolet through the visible [12].



The detectors are powered by a highly stable Fluke 412A, 0.5 to 2 kV continuously variable DC power supply. The adjustability feature allows for compensation for the shape of the photomultiplier response curve and further permits adjustment of readings for 100% T on the oscilloscope display.

Photomultiplier output is sent to an oscilloscope. Presently, a Hughes 105A Memoscope (storage oscilloscope) is being used with accompanying preamplifier module. The modules available are: 05-1 Wideband; 05-2 Dual trace; and 05-3 High Sensitivity. Display may be triggered internally, i.e., by the signal itself, or externally by a triggering device which has been built on.

Just completed and awaiting testing is a photomultiplier amplifier built by the Research Electronics Shop and based on a design of Harvey [13]. This will convert the photomultiplier signal into voltage, using a solid-state operational amplifier with an offset control which will allow measurement of a small fractional change in signal. There is also provision for the optional conversion of %T into absorbance (logarithmic).

## CALIBRATION

### Calibration Reactions

To check on the general reliability of the instrument and to look for various artifacts such as bubbles, schlieren, unequal delivery of the reagents, etc., (see the discussion under ERRORS) runs should be made on reactions of known rates to ascertain that the correct rate constants are indeed obtained.

1. The formation of the thiocyanatoiron(III) ion. Results in agreement with those of Below, et al. [14] may be obtained from mixing the following solutions: (1) 0.0010 M  $\text{Fe}(\text{NO}_3)_3$ , 0.010 M  $\text{HClO}_4$ , 0.384 M  $\text{NaClO}_4$ ; (2) 0.01 M  $\text{KSCN}$ . A suitable wavelength is 590 nm. A pseudo-first-order rate constant of  $48 \text{ sec}^{-1}$  should be obtained at  $25^\circ$

2. The dehydration of carbonic acid. This is most easily studied by the acidification of  $\text{HCO}_3^-$  with insufficient  $\text{H}^+$ ; the measurably slow rise in pH is due to the conversion of the acidic  $\text{H}_2\text{CO}_3$  to the pseudo-acid  $\text{CO}_2$ . Suitable solutions to mix are 0.02 M  $\text{NaHCO}_3$  and 0.01 M  $\text{HCl}$  containing  $3.4 \times 10^{-5}$  M bromthymol blue. A wavelength of 590 nm is satisfactory here also. At  $24.1^\circ\text{C}$  the observed rate constant is  $20 \text{ sec}^{-1}$  [11].

#### Transport Time

The transport time is the time during which reactants flow. Either of the calibration reactions may be used for this determination. The oscilloscope is triggered immediately before advancing the stepped cam to start a run. In this way the instant of injection, the entire transport period, and the instant of stopping all can be seen on the display. The transport period corresponds approximately to one of continuous flow and thus gives a nearly horizontal line for most of its duration.

#### Efficiency of Mixing

The effective mixing time can be estimated by observing the behavior in the instrument of an "instantaneous" reaction -- i.e., one considerably too rapid to be resolved. Typical would



be the triiodide-thiosulfate reaction or a Brønsted acid-base reaction observed with indicators. In the display, an apparently finite reaction time will be observed. The efficiency of mixing can then be reported in terms of the time required for an apparent 96% or 98% reaction [4, p 371].

## ERRORS

### Slit-length and Finite-mixing-time Errors

In stopped-flow equipment, since the flow channels are of small bore, observation across the channel allows only very short optical paths; hence the usual design, as followed in our present model, of observation along the channel. This means, however, that at the moment of stopping, the portions of fluid in different regions of the observation channel have different ages (times since mixing), and, in fact, the composition will not be truly homogeneous at any finite time. This has been called the slit-length effect [2, p 720]. (The corresponding slit-width effect, operative when observing across the channel, is clearly of much smaller magnitude.) It can be shown [15] that for first-order kinetics, no error is caused by the slit-length effect; that is, the correct half-time (or first-order rate constant) will be measured. For second-order kinetics there will be an error.

Closely related is the effect due to the fact that mixing is not instantaneous, and thus the time after the onset of mixing is not the "time of reaction" as given by the extent of reaction. Again, there is no error for first-order kinetics;

for second-order kinetics, where the "initial concentration" must be known, the error is significant if the half-time approaches the effective mixing time.

Lin and Rorabacher [16] have analyzed these two errors and have shown a way to correct the data in the case of second-order kinetics when the time of mixing is not considerably greater than the half-time.

Diffusion from one reservoir to another can be a significant error if the concentrations of reactants are of vastly different concentrations. It is a simple precaution, with our apparatus, to keep the needle valves closed except when runs are being made. Moreover, if a rapid series of shots is performed, effects due to diffusion should be seen chiefly in the earlier shots.

Inequality of flow.- The use of gas drive rather than syringe drive to force liquids out of the reservoirs could lead to unequal flow of the two reagents under two conditions, (1) if the viscosities of the two solutions are significantly different, and (2) if one of the flow channels leading from a reservoir to the mixer becomes partially or fully blocked by a particle inadvertently introduced.

Cavitation. - In turbulent flow, due to variations in pressure from point to point, cavitation may occur at regions of low pressure, leading to a stream of very fine bubbles with consequent turbidity and a large loss of optical transmittance. It is easily tested by discharging water at all the flow velocities to be used, looking for any changes in transmittance.



Air bubbles of larger size may cause errors of two sorts. If a bubble is trapped in the stopping cylinder, oscillations will occur when the flow stops, resulting in spurious oscillations of the observed signal. Air bubbles in the optical path will seriously decrease the transmission, and a bubble passing through the optical section could resemble a chemical event.

## APPENDIX A

### OPERATING CHARACTERISTICS OF THE MODEL IV REACTOR

1. Volume of reservoir<sup>a</sup>: 31 ml each
2. Volume of mixer<sup>a</sup>: 20  $\mu$ l
3. Volume of transfer tube<sup>a</sup>: 10  $\mu$ l
4. Volume of observation tube<sup>b</sup>: 131  $\mu$ l
5. Dead volume<sup>c</sup>: 95  $\mu$ l
6. Volume transferred per step of cam<sup>a</sup>: 1.51 ml
7. Transport time<sup>d</sup>: 45 msec at 60 psig of nitrogen;  
35 msec at 80 psig.
8. Volume flow rate<sup>e</sup>: 34 ml/sec at 60 psig; 43 ml/sec  
at 80 psig.
9. Linear flow velocity in 2-mm channel<sup>f</sup>: 10.7 m/sec  
at 60 psig; 13.8 m/sec at 80 psig.
10. Dead time<sup>g</sup>: 2.8 msec at 60 psig; 2.2 msec at 80 psig.

#### NOTES:

<sup>a</sup>Computed from the dimensions.

<sup>b</sup>Computed from the dimensions; includes additional volume due to the thickness of the Teflon washer.

<sup>c</sup>Volume from the first point of mixing to halfway through the observation tube.

<sup>d</sup>Time during which the reactants flow. Transport time was determined by direct measurement. The reactants in the storage reservoirs were  $\text{Fe}^{3+}$  and  $\text{SCN}^-$ . The oscilloscope was triggered immediately before advancing the cam, so that the instant of injection, the entire transport period, and the instant of stopping all could be seen on the display. The transport period



corresponds to one of steady flow and thus gives a nearly horizontal trace.

<sup>e</sup>Volume per step divided by transport time.

<sup>f</sup>Volume of flow rate divided by cross-section of tubing.  
The critical flow velocity for turbulence [A, p. 715] is about 0.1 m/sec.

<sup>g</sup>Dead volume divided by volume flow rate.

Remark:

A full series of 12 shots will require slightly in excess of 9 ml of each reagent.

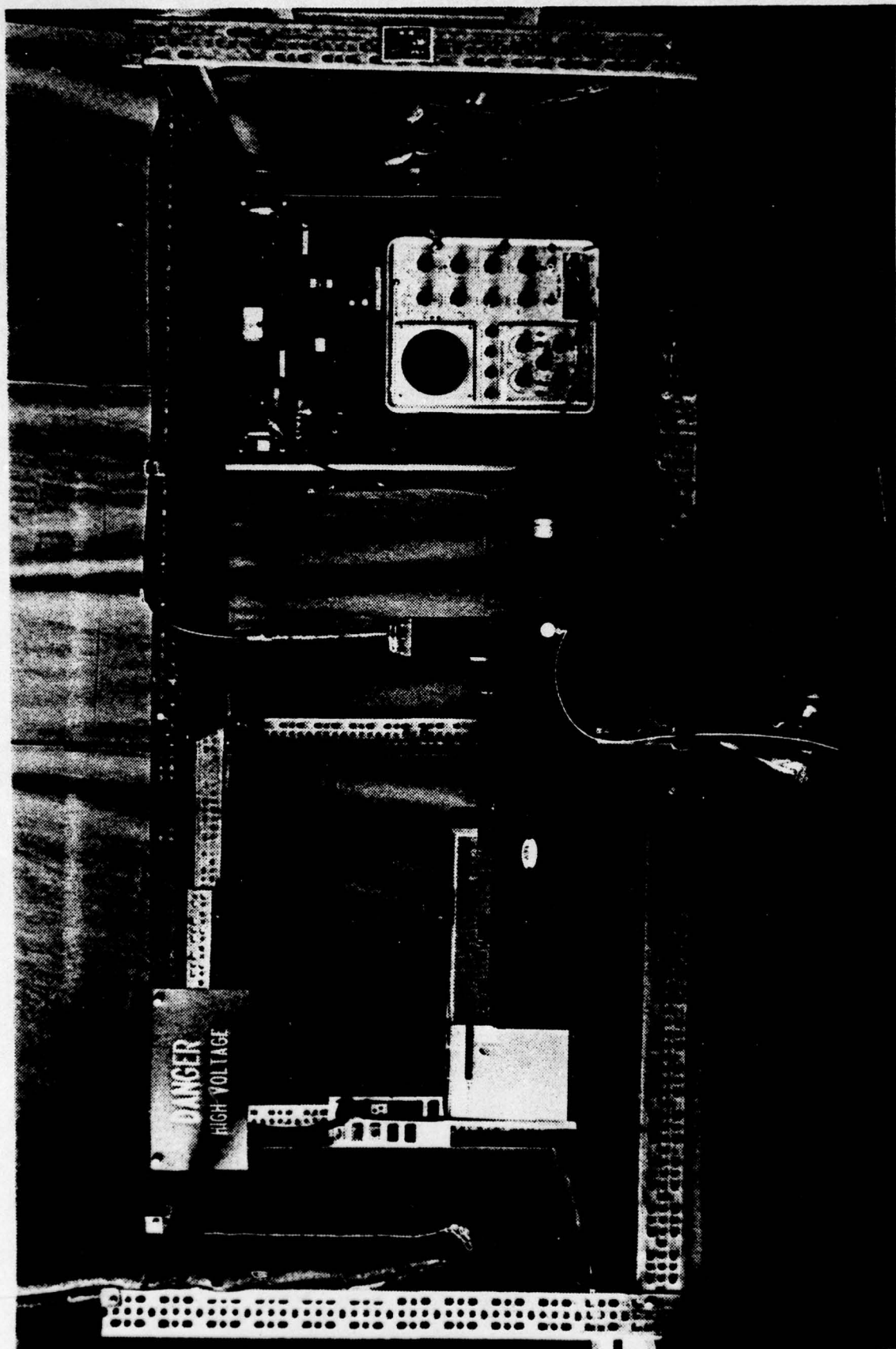


Figure 10. Overall View of Stopped-Flow Apparatus



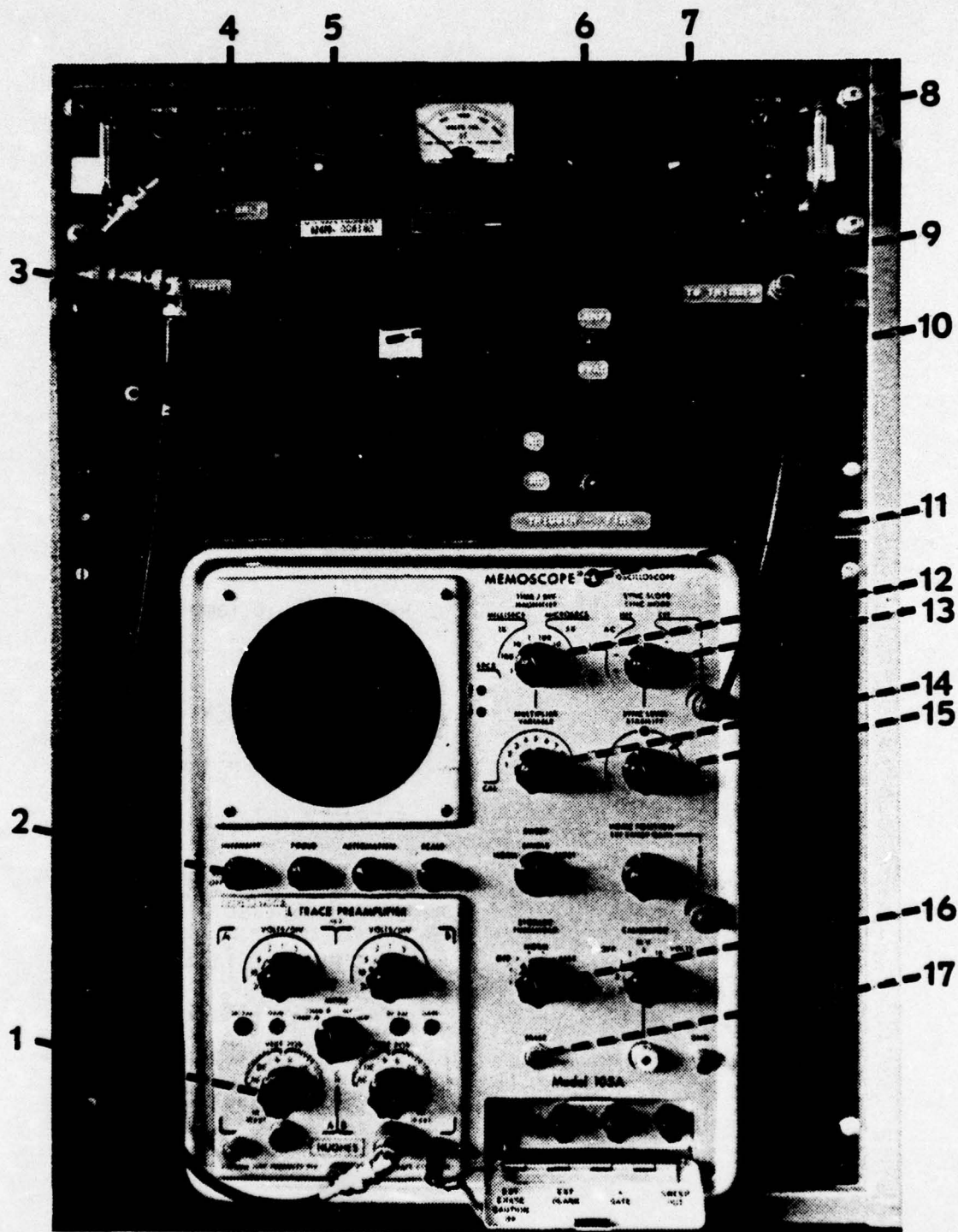


Figure 11. Detail of the Electronics Package

# KEY TO FIGURE 11

<u>Switch Number</u>	<u>Description</u>
1.	INPUT. SELECTOR (Black) and VERT POS (Red)
2.	INTENSITY/AC OFF
3.	ERASE
4.	POLARITY
5.	X100
6.	X10
7.	VERNIER
8.	PWR ON pilot lamp
9.	TRIGGER
10.	GROUND/0% TRANSMITTANCE
11.	OSCILLOSCOPE pilot lamp
12.	TIME/DIV (Black)
13.	SYNC SLOPE (Black) and SYNC MODE (Red)
14.	MULTIPLIER (Black)
15.	SYNC LEVEL (Black) and STABILITY (Red)
16.	STORAGE (Black) and THRESHOLD (Red)
17.	ERASE



## APPENDIX B

### DETAILED OPERATING INSTRUCTIONS

NOTE: For the location of the various switches mentioned below, refer to Figures 10 and 11.

#### A. WARM-UP (Allow 30 minutes)

1. Turn on MAIN POWER switches (2) at extreme left of the instrument rack.

2. Turn on POWER switch on the Beckman DU Power Supply. If the hydrogen lamp is to be used, turn the H<sub>2</sub> LAMP switch to "Warm up"; after at least five minutes, turn to the position of the highest number for which the lamp will fire. If the tungsten lamp is to be used, check to see if it is lighted by looking into the top of the lamp housing; if not, turn on the toggle switch at the rear of the lamp housing. (See Beckman DU Power Supply Manual for further details).

3. Check to see that the pilot lights for the electronic package are on. In the warm-up mode the Fluke Power Supply should have its POWER ON pilot lighted and the POLARITY switch set at "HV off". Illumination for the TRIGGER and GROUND push-buttons should be on. On the oscilloscope, the pilot light should be on (may be turned on by the INTENSITY knob); STORAGE to "Off"; INTENSITY to a level sufficiently low that the screen is not burned; SYNC MODE to "DC" and SYNC SLOPE to "EXT -". On the dual trace preamplifier, the INPUT SELECTOR (black) should

be set to "Normal, ground". The spectrophotometer shutter should be closed (pulled out to the first detent) during warm-up and also during all idle periods.

B. SETTING OF 0% AND 100% TRANSMITTANCE

1. Turn the WAVELENGTH knob on the spectrophotometer to the desired setting.

2. With the reservoir valves closed, stepping cam in the first position (stopping piston down), fill both reservoirs with the reference liquid (water or other appropriate medium) by removing filling-port plugs, inserting syringe needle through the ports to fill, then replacing plugs.

3. Place oscilloscope into free-run mode by turning the STABILITY switch clockwise until its pilot light shows, then increase INTENSITY until beam can be seen when TIME/DIV is set at "10 millisec". Turn VERT POS (red) to move beam to 0% T position (normally the top of the screen; parallax must be minimized) then turn INPUT SELECTOR (black) to "DC, normal".

4. Set the nitrogen pressure to the desired value (from 60 to 100 psig) and attach the quick-disconnect. Open the two reservoir valves simultaneously.

5. Turn the POLARITY switch on the Fluke power supply to "-" (right). Open the spectrophotometer shutter by pushing all the way in.

6. Turn one step on cam. Adjust voltage on the power



supply with switches X100, X10, and VERNIER until the oscilloscope trace rests on the 100% T position.

7. Repeat step 6 until the 100% T line is stable and there are no "blips" on the trace (evidence of bubbles).

8. If the last position on the stepping cam is reached and more observations are necessary, close both reservoir valves, open the drain valve and with the ramrod, push rapidly down on the stopping piston until the contents are expelled and the bottom position is reached. Close the drain valve, reset the cam to the first position, open the reservoir valves and continue steps 6 and 7 until a stable trace is obtained.

9. Alternately reset 0% T by pushing the blue GROUND button and readjusting VERT POS (red) and then 100% T with the high-voltage switches, as in step 6, until both positions are set.

10. Empty the reservoirs by opening the drain valve slowly (Note: There will be a surge of gas once the last of the liquid has drained from the reservoirs and mixer). Close the needle valves. Force down the stopping piston with the ramrod (as in step 8) rapidly. Look for evidence of bubbles in the drain line. Close the drain valve and reset the cam to the first position. Depressurize the system by means of the quick-disconnect.

### C. REACTION OBSERVATION

NOTE: IT IS IMPERATIVE THAT YOU DO NOT CHANGE THE WAVELENGTH, SLIT OPENING, HIGH VOLTAGE SETTING, OR VERTICAL AMPLIFIER SETTING AFTER DETERMINING 0% AND 100% TRANSMITTANCE.

1. With the system depressurized and the needle valves closed, remove the filling port plugs.

2. Measure out precisely equal volumes (19-31 ml each) of the two reactant solutions and load them through their respective filling ports, being careful not to squirt any reactant into the pressure equalization channel.

3. Insert the filling port plugs.

4. Open the needle valves together.

5. Pressurize the system by connecting the quick-disconnect fitting.

6. Shoot two or three shots to sweep out any bubbles (observe the oscilloscope trace for noise) and run the rest of the first series of shots to rinse out any diluent left in the instrument from the 0-100% T calibration.

7. Close the needle valves, open the drain valve, empty the stopping cylinder with the ramrod, reset the cam to starting position, close the drain valve and re-open the needle valves. The system is now ready to run kinetic shots.

8. On the oscilloscope set STORAGE to "Norm" and adjust THRESHOLD such that when a trace is swept across the screen (by pressing TRIGGER) the path of the beam is fully retained. Press ERASE. Set SYNC SLOPE to "Int -". Adjust SYNC LEVEL and STABILITY so that opening and closing the shutter will trigger the sweep. Press ERASE.



9. Turn the cam one step and observe whether the time base is such that the entire event is seen. If not, adjust TIME/DIV and MULTIPLIER appropriately.

10. ERASE. Turn the cam one step. Observe the oscilloscope screen. Photograph the screen with the Polaroid CR-9 camera. Repeat until the first series of shots is used up.

11. To run the next series of shots for the same reaction, repeat steps 7 and 10. Once reservoirs are depleted, repeat steps 1 through 7 and 10.

#### SOME OPERATING PRECAUTIONS

- ▷ Before emptying the stopping cylinder, first close the reservoir valves. Only then should the exhaust valve be opened.
- ▷ After the stopping cylinder has been emptied, three operations must be checked before starting a new series of runs (assuming the reservoirs do not need refilling): Close the exhaust valve; reset the cam to the first position; last, open the reservoir valves.
- ▷ In refilling the reservoirs, disconnect the pressure system and close the reservoir valves before removing the filling-port plugs.

#### STAND-BY PROCEDURE

- ▷ Close the shutter (even for relatively short idle periods).
- ▷ On the oscilloscope, turn INTENSITY down, STORAGE off, press ERASE.
- ▷ On Fluke power supply, turn POLARITY to "HV Off".
- ▷ On Beckman Power supply, if hydrogen lamp is in use, turn H<sub>2</sub> LAMP to "Warm up".

### SHUT-DOWN PROCEDURE

- ▷ 1. Follow the first three steps under STAND-BY PROCEDURE.
- ▷ 2. On the Oscilloscope, turn INPUT SELECTOR (black) to "Norm, ground".
- ▷ 3. On the spectrophotometer power supply, turn H<sub>2</sub> LAMP to "Off" and turn POWER to "Off".
- ▷ 4. Turn off both main power switches.
- ▷ 5. With the stopped-flow reactor still under pressure, open the reservoir valves and cautiously open the exhaust valve to blow out the contents. Close the reservoir valves and empty the stopping cylinder. Leave the stepping cam in its last position.
- ▷ 6. Depressurize, remove the filling-port plugs, and fill both reservoirs with water.
- ▷ 7. Repressurize and open the reservoir valves to force water through the mixer and into the stopping cylinder. If further rinsing is felt desirable, steps 5, 6, and 7 may be repeated.
- ▷ 8. Leave system full of water and reservoir valves open.
- ▷ 9. Disconnect the pressure system and turn off the nitrogen tank at the main valve.

### DATA REQUIRED

1. The following data should be placed on each photograph:

Timebase: \_\_\_\_\_ msec/division

Location of 0% and 100% Transmittance

The reaction being studied and the concentrations used.

Date, photo number, and lab book reference



2. To reproduce a run at a later time, one will need to record in the notebook the following data:

All information on the photograph  
Slit width  
Wavelength  
Source used  
HV setting  
Bandwidth of the system  
Calibrant for setting 0 and 100% T  
Detector  
Type of triggering  
Temperature of the reactants  
Composition of the reactants  
Nitrogen gas pressure

## APPENDIX C

### PARTS LIST AND SUPPLIERS

#### MATERIALS:

Teflon, extruded rod

Cadillac Plastics and Chemical Co.  
313 Corey Way  
So. San Francisco, CA 94080

Stainless Steel Rod (316)

Pacific Metal Fabricators  
3383 Livona Avenue  
Los Angeles, CA 90034

Plexiglass/Lucite, 4 inch thick acrylic plastic

Rohn and Haas Company  
Independence Mall West  
Philadelphia, PA 19105

Fused Silica Windows, .875 inch diameter by .0625 inch thick

Quartz Scientific Incorporated  
34602 Lakeland Blvd.  
Eastlake, Ohio 44094

#### HARDWARE:

Flexible gas line, PN 482-12

E. Edelman and Company  
4711 Golf Road  
Skokie, Ill 60076

Threaded fittings and quick disconnect gas fittings (Swagelok)

Van Dyke Valve and Fitting Co.  
1240 Birchwood Drive  
Sunnyvale, CA 94086

Syringes, BD- 20 ml

A. H. Thomas Co.  
Vine Street at Third  
P. O. Box 779  
Philadelphia, PA 19105



Linear Travel Bearings

Thomson Bearing Co.  
Dept 10  
Manhasset, NY 11030

BNC Fittings, PN 31-4320 Crimp

Bunker Ramo Corporation  
Amphenol Connector Division  
2801 S. 25th Avenue  
Broadview, IL 60153

Coaxial Cables, RG 58/U, PN 01166

Columbia Electronic Cables  
11 Cove Street  
New Bedford, MA 02744

Triggering circuit batteries, Burgess U15 ~ 22.5 volts

Gould Incorporated  
Battery Division  
467 Calhoun Street  
Trenton, NJ 08607

ELECTRONICS:

Photomultipliers ~ 7102, 6810A and 4832

RCA  
Solid State Division  
4546 El Camino Real  
Los Altos, CA 94022

Photomultiplier Housing for 7102

Eldorado Electronics  
2821 10th Street  
Berkeley, CA 94704

Photomultiplier Power Supply ~ PN 421A

John Fluke Mfg. Co.  
P. O. Box 7428  
Seattle, WA 98113

Storage Oscilloscope - Mdl 105A

Hughes Aircraft Company  
Vacuum Tube Products Division  
2020 Oceanside Blvd.  
Oceanside, CA 92054

## REFERENCES

- [1] M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry", A. Weissberger, ed., Interscience, New York, 1963, Vol VIII, Part II, Chap XVIII.
- [2] F. J. W. Roughton and B. Chance, ibid., Chap XIV, pp 703-748.
- [3] Q. H. Gibson in "Fast Reactions", K. Kustin, ed., Methods in Enzymology, 16, pp 187ff.
- [4] E. F. Caldin, "Fast Reactions in Solution", Wiley, New York, 1964.
- [5] H. Hartridge and F. J. W. Roughton, Proc. Roy. Soc., A104, 376 (1923).
- [6] F. J. W. Roughton, ibid., B115, 473 (1934)
- [7] B. Chance, J. Frank. Inst., 229, 455 (1940).
- [8] Q. H. Gibson, J. Physiol., 117 49P (1952).
- [9] Q. H. Gibson and L. Milnes, Biochem. J., 91, 161 (1964).
- [10] R. L. Berger, B. Balko, H. F. Chapman, Rev. Sci. Inst., 39, 493 (1968).
- [11] Aminco-Morrow Stopped-Flow Apparatus, Operating Instructions (Cat. 4-8409, Instruction No. 939-B), American Instrument Co., Silver Spring, Maryland, Sept., 1971.
- [12] RCA Chart PIT 701B, RCA Electronic Components Div., Harrison, N. J., 1970.
- [13] R. A. Harvey, Analyt. Biochem., 29, 58 (1969).
- [14] J. F. Below, Jr., R. E. Connick, C. P. Coppel, J. Am. Chem. Soc., 80, 2961 (1958).
- [15] J. E. Stewart, Durrum Application Notes, No. 4, Durrum Instrument Co., Palo Alto, California, 1971.
- [16] C. Lin and D. B. Rorabacher, J. Phys. Chem., 78, 305 (1974).



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